DOE PROOF-OF-CONCEPT DIRECT COAL LIQUEFACTION PROGRAM
Activity of Recovered Catalysts from POC Run No.1

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INTRODUCTION
In POC Run No. 1 HRI's Catalytic Two-Stage Liquefaction (CTSL) process was evaluated using Illinois No. 6 coal from Crown II Mine in a 3 ton/day process development unit. Solid Separation was accomplished using a vacuum still and subsequently switched to a Kerr McGee residual oil solvent extraction unit (ROSE-SR^{SM}). Akzo AO-60 1/16" extrudate catalyst, a Ni/Mo supported catalyst, was used in both stages. The temperature of the first stage reactor was in the range of 407° to 414°C and about 16° to 27°C lower than that of the second stage. Throughout most of the 57 days operations, catalysts were added and withdrawn from each reactor to maintain consistent process performance. In this paper the activity of the withdrawn catalysts from both reaction stages at selected operation periods is discussed in respect to the degree of carbon lay down and total contaminations.

EXPERIMENTAL
The catalytic activity of fresh and withdrawn catalysts was characterized by its ability to convert a resid containing coal derived liquid to lighter products using a 20 cc shaking microautoclave reactor. As a common test oil the filtered liquid (227-55-23A PFL) that had been obtained during the CTSL Bench Unit operations with Black Thunder Mine coal of Period 23A of Run 227-55, was used. The experiments were all carried out with 13.8 MPa hydrogen pressure, and 30 minutes time after insertion of the autoclave into a fluidized sand bath heater maintained at 440°C. At the end of this time the temperature of autoclave was dropped rapidly by plunging the autoclave into a water bath. The catalyst tested was held in a wire basket in the autoclave and catalyst-oil contact was promoted by the vertical agitation of the autoclave during the experiment. Each experiment used 2 grams of the test oil, and, usually, an amount of oil-free catalyst (toluene extracted) that corresponded to 2 grams of uncontaminated fresh catalyst after correction for the estimated contaminant content, so that the experiments had an approximately common severity of around 30 minutes x grams uncontaminated catalyst/gram test oil.

The product oil was washed from the autoclave and the catalyst using THF as a wash solvent. The THF was removed from the washings by vacuum evaporation using a roto-evaporator in a hot oil bath at 46°C. The residual oil (524°C+) content in the reference oil and product oils were determined by using a TGA procedure.Typcially, the 227-55-23A PFL reference oil containing 29.6 W% 524°C+ residual oil, as determined by ASTM D-1160 procedure, was reported as having 29.6-30.6 W% residual oil content by TGA analysis. Several analyses were performed to determine the amount of contaminants on the oil-free catalysts withdrawn during the POC program. These analyses were bulk and particle densities, elemental (CHNS), ignition loss and major metals (Mo, Ni, Fe, Na, Ca).

CARBONACEOUS AND OTHER CONTAMINANTS
Considering four possible methods of using different analyses (particle density, sum of individual contaminants, nickel and molybdenum content) for estimation of the actual contaminant content in the catalysts, these methods do not agree very closely, as follows comparing the average results for the 13 cases where all of the four methods could be used.

Nickel	47.3%	Molybdenum	46.8%
Particle Density	32.6%	Total Measured Contaminants	25.9%

The Ni and Mo analyses appear to be erratic, with a possibility the Mo and Ni contents of the fresh catalyst are not as high as the cited analyses. The difference in apparent contaminant content based on particle density and contaminants analyses, by an average of 6.7% more contamination indicated by the particle density values, could have been caused by failure to determined all of the metallic contaminants. Titanium content of one of the sample (Period 26), which proved to be higher than the Fe, Na, and Ca contents of the first stage catalyst and also higher than the average of those others elements in the second stage catalyst, have been determined. However, the amounts of Ti (as TiO$_2$) were only 1.6 and 0.7 W%, which were considerably less than the above difference in indicated total contaminants content. *Figure 1* compares the amounts of catalyst contamination, Period by Period, based on the latter methods. The actual contaminants analyses persistently indicated more

contamination of the second stage catalyst, but the catalyst density values indicate more contamination of the first stage catalyst. Because it was uncertain that all of the contaminating constituents had been determined by chemical analyses, and uncertainty concerning the reliability of such analyses, the estimated fresh catalyst contents that were used were those indicated by the particle density measurements.

CATALYST ACTIVITIES
The activity of the tested catalysts are expressed as percentage of that of a reference catalyst. The reference catalyst was Criterion C-317 catalyst that had been presulfided with a TNPS/gas oil mixture using a fixed bed. The nominal accuracy of the tests was estimated on the basis of the four pairs of replicate tests, as follows:

Test No.	Catalyst	Relatives Activities (%)	Oil Recovery (%)
72 & 73	Fresh AO-60	70, 70	94, 92
90 & 91	Presulfided AO-60	167, 164	89, 90
99 & 104	Period 33 1st Stage	98, 98	92, 100
97 & 103	Period 33 2nd Stage	62, 62	88, 98

The charge catalyst to Run POC-01, Akzo AO-60 catalyst, when not presulfided was of lower activity (70%) than the reference catalyst. Upon presulfidation with dimethyl disulfide or thiononyl polysulfide in tetralin increase the catalyst to 164-167% of the reference catalyst. Similar observation was obtained when Shell S-317 catalyst was presulfided. It's activity increased to 182% of the reference catalyst.

Figure 2 compares the activities of withdrawn catalysts from various periods of Run POC-01. The first samples, Period 1, were less active, 50-62% of the reference activity, than the fresh (unpresulfided) AO-60 catalyst. This pattern was caused by incomplete presulfiding and accumulating of contaminants on the catalysts. These catalysts contained only 35-53% of theoretical sulfur content as compared to values averaging 97% of theoretical sulfur content for catalyst samples later in the run. The activities of the catalysts can be grouped into two regions corresponding to the changes in the operating conditions. In the initial period, Periods 4 to 20, the first and second stage catalysts ranged from 88 to 104 % of the activity of the reference catalyst. There were no on-line catalyst addition/withdrawal in the first 9 operating periods, during which the aging of the catalysts were accelerated to the equilibrium values. Catalyst addition/withdrawals were initiated in Period 10 but on reduced rates on alternate days basis (0.5 lb/ton coal tot he first stage and 1.0 lb/ton coal tot he second stage). The first and second stage temperatures ranged from 399° to 407°C and 427° to 432°C, respectively. Also, the unit was in an ashy recycle mode in the initial periods and was phased out gradually when the ROSE-SR^{SM} solid separation unit was introduced since Period 13. Solid-free recycle mode was implemented from Period 21 onward.

Catalyst samples from the later periods, Periods 26 to 57, were of relatively low activity at 59-72% of the reference catalyst activity. In these later periods, coal feed rate was increased 50% with higher reactor temperatures. The first and second stage temperature were raised by approximately 3° and 5° to 8°C, respectively to cope with the higher coal feedrate. These higher temperatures resulted in higher coke lay down on the catalyst, especially that of the second stage catalyst, as shown in *Figure 3*. Also, starting from Period 20, catalyst addition rates were increased to target equilibrium values of daily additions of 1.5 and 3.0 lb/ton to first and second stages, respectively.

With the exception of Period 1 catalyst, the activities of the other catalyst samples were largely related to the degree of contamination, as shown in *Figure 4*. A correlation considering contents of both carbon and other contaminants gave the following equations:

$$\text{Relative Activity} = A + B * W_{carbon} + C * W_{others}$$

	A	B	C	Confident Limited (%)
All Catalysts	187.4	-5.11	2.72	>99.99
Without Presulfided Catalysts	179.7	-4.82	2.44	99.91

where, W_{carbon} and W_{others} are the weight percent of carbon and other contaminants on the catalysts, respectively. Despite the lower catalyst replacement rate to the first stage (by a factor ½), first stage

catalysts were generally more active than the second stage catalysts by an average of 7%. The relative activity of the first and second stage catalysts appears to be related principally to the lower content of carbon on the first stage catalyst and not to the total amount of contaminants. Excepting the Period 1 catalysts, where the first stage and second carbon contents were virtually the same, in the other six pairs of first and second catalysts (as given in *Figure 3*) the second stage catalyst contained more carbon, by 0.8 to 7.8 W%. The following tabulation gives average values of these factors for the first and second stage catalysts that have been tested:

Stage	Catalyst Activity	Carbon Content (%)	Catalyst Content (%)
First	80	14.56	73.0
Second	72	17.93	75.0

The multiple correlations summarized above indicated that the average activity of the first stage catalysts would be 4% higher than that of the second stage catalysts.

COMPARISON OF EVALUATIONS WITH PROJECTED ACTIVITIES
The residual oil yields in CTSL Bench Unit coal liquefaction operations have been correlated as being dependent on catalyst age by a functionality that assumed catalyst activity declined by a constant proportion for each day of operations at the liquefaction conditions. Projections were calculated for the first and second stage catalyst activities during the course of Run POC-01, using the actual pattern of catalyst addition/withdrawal that occurred during the run. In these calculations, the catalyst deactivation factors for the two stages were based on those given in the Final CTSL topical report. For the interval of Run POC-01, Period 26 through 43, during which equilibrium catalyst addition rates were maintained the average of the microautoclave catalyst evaluation results were lower for the first stage catalyst, and higher for the second stage catalyst, than the projected values. The trends in the evaluated caalyst activities for this interval of the run were directionally in agreement with of those of the projections, showing a possible small decline in the first stage catalyst activity and essentially no change in second stage catalyst activity.

However, the evaluation results differ even more markedly from the projected values for the first interval of the run before Period 20 where there were low rates of catalyst addition to "aged" the initial charge of catalysts, and for the final interval of the run after Period 45 where there was no catalyst addition to the second stage with reduced catalyst input to the first stage.

Figure 5 summarizes the results of calculations for projection activities using the first and second stage deactivation factors adjusted to give a close fit to the evaluations for Periods 26, 32, and 43. This figure also includes the experimental evaluations throughout the run. The adjustments of the deactivation factors were approximately 42% higher for the first stage and 51% lower for the second stage, as compared with he CTSL Bench unit factors.

SUMMARY AND CONCLUSION
The un-presulfided form, "fresh", of Akzo AO-60 catalyst was 2.5 times less active in term of converting to lighter products. Due to the addition of "fresh" catalyst directly into the reactor, the equilibrated catalyst activity was only half of the fully presulfided fresh catalyst, while the second stage equilibrated catalyst was even lower and was similar to that of the un-presulfided fresh catalyst. These microautoclave evaluation results correlated with carbon content of the catalyst, and more strongly with total contamination, including metal contamination. A multiple regression correlation indicated significant effects of both carbon content and other contaminants with the greater impact of the carbon content.

ACKNOWLEDGMENT

FIGURE 1

CONTAMINATION OF CATALYST DURING RUN POC-01

Basis Particle Density or Contaminants Analyses
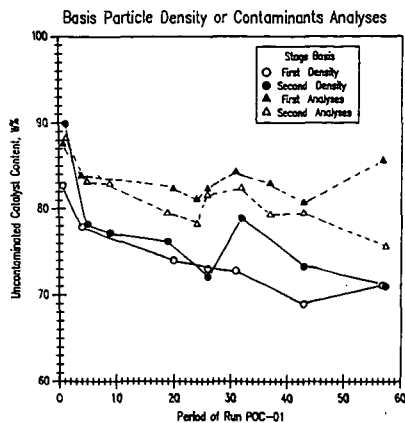
FIGURE 2

RELATIVE ACTIVITY OF RUN POC-01 CATALYSTS

MA Eval. – Analyses THF, Ash-Free Adj. for Excess Oil

Tests With Very High Recoveries Discarded
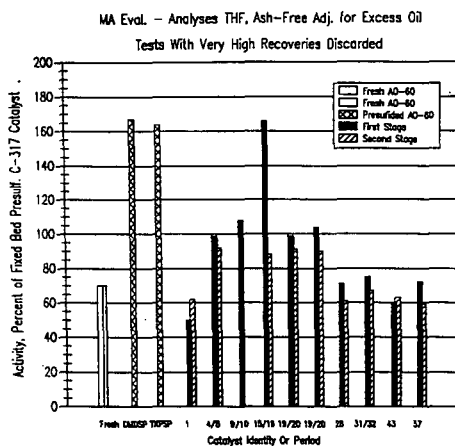

FIGURE 3

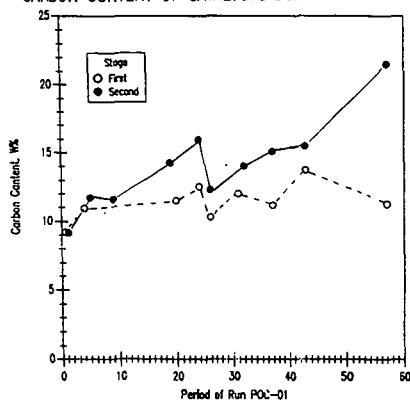## CARBON CONTENT OF CATALYSTS DURING RUN POC-01

FIGURE 4

ACTIVITY OF POC–01 CATALYSTS IN MICROAUTOCLAVE TESTS

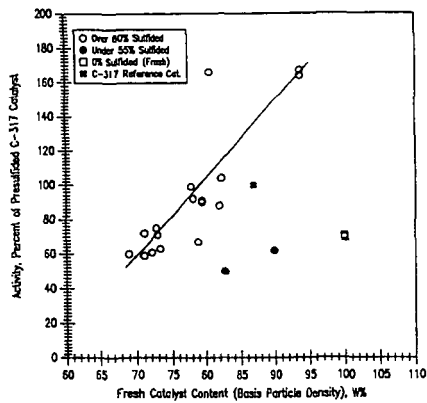Versus Contamination (Basis Particle Density)

FIGURE 5

POC–01 CATALYST ACTIVITY – EVALUATIONS AND PROJECTIONS

Deactivation Factors to Fit Period 26 to 43 Results